coordinate of roller surface; β',change of β coordinate from material entrance into deformation region and to its outlet; $\beta_+ = 2 \arctan (x_+/a)$ entrance coordinate; β_-, outlet coordinate; ρ, density; λ, thermal conductivity; c_V, heat capacity; T_1, T_2, temperatures of roller surfaces; 2Q, material discharge; V, speed of roller surface rotation.

LITERATURE CITED

1. J. M. McKelvey, Polymer Processing, Wiley, New York (1962).
2. A. G. Frederickson, Principles and Application of Rheology, Prentice Hall, Englewood Cliffs, New Jersey (1964).
3. M. J. Finston, J. Appl. Mech., 18, No. 12 (1951).
4. H. Schlichting, Boundary Layer Theory, McGraw-Hill, New York (1960).
5. N. G. Bekin, R. V. Torner, V. Yu. Petrushanskii, and A. I. Sakhaev, Kauchuk i Rezina, No. 6 (1971).
6. N. V. Roze, Inzh.-Fiz. Zh., 17, No. 2 (1970).
7. V. V. Litvinov and N. G. Bekin, in: Machines and Technology for Processing Synthetic Rubber and Polymers [in Russian], Part 1, Yaroslavl' (1974).
8. N. A. Lavrent'ev and B. V. Shabat, Methods of the Theory of Functions of a Complex Variable [in Russian], Nauka, Moscow (1973).

INFLUENCE OF GRAVITATIONAL CONVECTION ON THE PROGRESS OF A HETEROGENEOUS CATALYTIC REACTION UNDER ISOTHERMAL CONDITIONS

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The critical conditions for origination of natural gravitational convection during the progress of a heterogeneous catalytic reaction are considered. The influence of developed convection on the reaction progress under isothermal conditions is analyzed.

As is known, the macroscopic velocity of a heterogeneous catalytic reaction depends on the relationship between the true reaction rate constant and the intensity of mass transfer [1]. The intensity of mass transfer evidently increases in the presence of gravitational convection. This can result in the passage from one mode of reaction progress to another. In other words [if the reaction were to proceed in the diffusion domain without natural convection and the rate of mass transfer were limited] then the reaction rate can set the limiting stage for sufficiently strong convection.

This paper is devoted to a clarification of the role of natural gravitational convection in the progress of a heterogeneous catalytic reaction. However, the solution of this question requires knowledge of the conditions for origination of gravitational convection due to the progress of a heterogeneous catalytic reaction.

1. Critical Conditions for Origination of Convection

Let us consider an infinite plane horizontal layer filled with fluid or gas and bounded by solid boundaries. The temperatures on the boundaries are identical and do not vary with time. A catalytic reaction of the type

$$\nu_1 A_1 \xrightarrow{K} A_2 \tag{1}$$

proceeds on the upper boundary of the layer, where A_1 is the provisional notation for the initial material, A_2

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is the reaction product, ν_1 is the stoichiometric factor, and K is the reaction rate constant at a given temperature.

A constant concentration of initial material is maintained on the lower boundary. Therefore, a binary mixture will henceforth be considered. In this case, the density should depend on the concentration of one of the reaction components. The density of a binary mixture for a gas can be expressed as follows:

$$\rho = \frac{\rho_0}{1+\alpha a}, \tag{2}$$

where

$$\rho_0 = \frac{p}{RT}\cdot\mu_1; \quad \alpha = \frac{\mu_1-\mu_2}{\mu_2}.$$

If $\alpha > 0$, then a lighter product is obtained as a result of the reaction (decomposition reaction), while $\alpha < 0$ corresponds to the formation of a heavy product. Since the concentration a refers to the reaction product (1), then $\alpha < 0$ in the case under consideration. Considering a perturbation of the state for which there is no reaction product ($a = 0$), the gas density can be represented in a linear approximation as

$$\rho = \rho_0(1-\beta a), \tag{3}$$

where

$$\beta = -\frac{1}{\rho_0}\left(\frac{\partial\rho}{\partial a}\right)_T.$$

Since the reaction on the upper boundary is considered, then convection under isothermal conditions can originate only during the progress of a reaction with the formation of a heavy product (polymerization type reaction). Perfectly analogous results should be obtained in examining a decomposition reaction on the lower boundary of the layer. Taking into account that $|\alpha| < 1$ and $a < 1$, the dependence (2) can be represented approximately as

$$\rho \cong \rho_0(1-\alpha a); \tag{4}$$

then $\beta = \alpha$.

In case a reaction with a liquid phase is examined, the density must be determined by means of (3), and the quantity β should be found experimentally. It should be noted that a reaction with a liquid phase will proceed with a change in volume, which involves taking account of the dependence of the characteristic size of the domain on the degree of conversion. Hence, a reaction in a gas will henceforth be examined.

The system of equations describing the process for origination of convection in a Boussinesq approximation [2] and taking account of (4) is

$$\begin{gathered}\frac{\partial\vec{v}}{\partial t} + (\vec{v}\vec{\nabla})\vec{v} = -\frac{\vec{\nabla}p}{\rho_0} + \nu\Delta\vec{v} + \vec{g}\alpha a;\\ \frac{\partial a}{\partial t} + \vec{v}\cdot\vec{\nabla}a = D\Delta a;\\ \operatorname{div}\vec{v} = 0.\end{gathered} \tag{5}$$

The boundary conditions are the following:

$$z = 0;\ \vec{v} = 0;\ a = 0;\ z = h;\ \vec{v} = 0;\ D\frac{\partial a}{\partial z} = K(1-a). \tag{6}$$

It should be noted that the assumption that the dependence of the density on the coordinates is negligible in the diffusion equations is justified sufficiently only for small α and for the reaction proceeding in an almost kinetic mode.

The stationary equilibrium conditions of the mixture under consideration are

$$\vec{v} = 0;\ \vec{\nabla}a_0 = A\cdot\vec{i} = \frac{\gamma}{\gamma+1}\cdot\vec{i},$$

where $\gamma = K\cdot h/D$; $\vec{i}$ is a vector directed opposite to the vector $\vec{g}$; A is the concentration gradient, and a_0 is the concentration under equilibrium conditions.

The parameter γ characterizes the ratio between the reaction rate and the diffusion rate [1], where $\gamma \gg 1$ corresponds to the reaction proceeding in the diffusion mode. For $\gamma \ll 1$ the reaction proceeds in the kinetic mode. It is easy to show that the principle of monotonicity of the perturbations [3] is satisfied for the problem under consideration. Hence, the conditions for the origination of convection are determined from the boundary-value problem for the stationary perturbation amplitudes (to first order):

$$-\vec{\nabla} p + \mathrm{Sc}\cdot\Delta\vec{v} + \mathrm{R}\,a\cdot\vec{i} = 0;$$

$$\mathrm{Sc}\,A\,(\vec{v}\cdot\vec{i}) = \Delta a; \tag{7}$$

$$\operatorname{div}\vec{v} = 0$$

with the boundary conditions

$$\xi = 0;\ \vec{v} = 0;\ a = 0;\ \xi = 1;\ \vec{v} = 0;\ \frac{\partial a}{\partial \xi} = -\gamma a. \tag{8}$$

The quantities h, $\rho_0(\nu D/h^2)$, ν/h are selected, respectively, as the distance, velocity, and pressure scales. The system of equations (7)-(8) is perfectly analogous to the equations describing the process for the origination of thermal convection if the concentration is replaced by the temperature, and the parameter γ, by the Biot number [4]. Eliminating the pressure from the first and third equations of the system (7), we obtain an equation containing only the vertical component of the velocity vector v_ξ. After substituting particular solutions of the form

$$v_\xi = w(\xi)\exp i(k_1x + k_2y);\quad a = a(\xi)\exp i(k_1x + k_2y)$$

into these equations, we obtain the system of equations

$$\mathrm{Sc}\left(\frac{d^2}{d\xi^2} - k^2\right)^2 w = \mathrm{R}\,k^2 a; \tag{9}$$

$$\mathrm{Sc}\,Aw = \frac{d^2a}{d\xi^2} - k^2 a \tag{10}$$

with the conditions on the boundaries

$$\xi = 0;\quad w = \frac{dw}{d\xi} = 0;\quad a = 0; \tag{11}$$

$$\xi = 1;\quad w = \frac{dw}{d\xi} = 0;\quad \frac{da}{d\xi} = -\gamma a. \tag{12}$$

The k_1 and k_2 in these expressions are real wave numbers characterizing the periodicity of perturbations along the horizontal coordinates x and y, $k^2 = k_1^2 + k_2^2$. Let us seek the solution of (9)-(10) by the Bubnov–Galerkin method [4, 5]. It should be noted that the use of this method to find the critical Rayleigh number yields very high accuracy when using just one basis function in the velocity approximation [4]. The error in determining the critical Rayleigh number for a plane horizontal layer in the case of thermal convection is ~0.5%.

Let us take the function

$$w(\xi) = \xi^2(1-\xi)^2.$$

as the basis function satisfying the boundary conditions. Substituting this expression into (10) and integrating, we find the form of the function $a(\xi)$:

$$a = C_1 \operatorname{sh} k\xi + C_2 \operatorname{ch} k\xi + \frac{\mathrm{Sc}\,\gamma\xi^2(1-\xi)^2}{k^2(\gamma+1)} + \frac{2\,\mathrm{Sc}\,\gamma}{(\gamma+1)k^6}\left[6k^2\xi(\xi-1) + 12 + k^2\right]. \tag{13}$$

The constants C_1 and C_2 are found from the boundary conditions (11) and (12):

$$C_1 = \frac{\mathrm{Sc}\,\gamma}{(\gamma+1)}\left\{\frac{2(12+k^2)\left[k\operatorname{sh}k + \gamma(\operatorname{ch}k - 1)\right] - 12k^2}{k^6(k\operatorname{ch}k + \gamma\operatorname{sh}k)}\right\};$$

$$C_2 = -\frac{2\,\mathrm{Sc}\,\gamma(12+k^2)}{(\gamma+1)k^6}. \tag{14}$$

Substituting $w(\xi)$ and $a(\xi)$ into (9), multiplying by $w(\xi)$, and integrating with respect to ξ between 0 and 1, we obtain the formula for the critical number R:

$$S = \mathrm{R}\frac{\gamma}{\gamma+1} = \frac{A}{B + 1260\,k\,(C_1D + C_2E)}. \tag{15}$$

Here

$$A = k^4(k^4 + 24k^2 + 504);\quad B = k^4 - 12k^2 + 504;$$
$$D = (12+k^2)(\operatorname{ch} k - 1) - 6k \operatorname{sh} k;\quad E = (12+k^2)\operatorname{sh} k - 6k(\operatorname{ch} k + 1).$$

Equation (15) yields the critical Rayleigh number as a function of the wave number k and the parameter γ. The dependence R(k) has a minimum at $k = k_*$ for a fixed value of γ. The critical Rayleigh number $R_*(\gamma)$ corresponds to this value of k_*. Taking account of the above-mentioned analogy, values of the complex $S_* = R_*[\gamma/(\gamma+1)]$ are obtained for different γ from the results presented in [4] (Table 3). It can be seen that $S_* = 1708$ for $k_* = 3.11$ as $\gamma \to \infty$. This agrees with the value of the critical Rayleigh number for thermal convection in a horizontal fluid layer bounded by solid surfaces. Indeed, as $\gamma \to \infty$ (diffusion mode of reaction progress) it follows from (6) that $a_0 = 1$ ($a = 0$) as $\xi = 1$, i.e., the problem goes over completely into the known problem on thermal convection. Depending on γ, the parameter S_* varies between 1708 and 1305 (for $\gamma \to 0$). Therefore, as γ diminishes, the value of R_* grows and $R_* \to \infty$ as $\gamma \to 0$. Physically, this means that for small γ the process is limited by the reaction rate, and the concentration of the product on the reaction surface tends to zero as $\gamma \to 0$, i.e., no difference in concentration originates due to the origination of convection. To ~0.5% accuracy, the dependence of R_* on γ can be described by the following approximate formula:

$$R_* = \frac{1305(\gamma+1)}{\gamma}\left[1 + \frac{0.309\gamma}{\gamma + 3.22}\right]. \tag{16}$$

2. Influence of Developed Convection on the Progress of a Heterogeneous Chemical Reaction

As above, let us consider a plane horizontal layer of a reacting gas with the boundary conditions (6), where $R \gg R_*$, i.e., intensive mixing occurs within the layer because of the concentration chemical convection which originates.

To clarify the influence of convection on a heterogeneous reaction, let us use the method of an equiaccessible surface [1] and let us introduce some mean product concentration θ in the volume. A change in the concentration θ can occur only because of the difference in the mass flows through the upper and lower surfaces, i.e.,

$$V\frac{d\theta}{dt} = (j_1 - j_2)s, \tag{17}$$

where $j_1 = \varkappa_1(a_+ - \theta)$; $j_2 = \varkappa_2\theta$; j_1 and j_2 are the mass flows, respectively, from the upper and to the lower surfaces; V is the volume under consideration; s is the surface; a_+ denotes the concentration of the reaction product on the reaction surface ($z = h$).

In the quasistationary approximation, the concentration on the boundary a_+ is determined from the condition of equal mass flow and reaction rate:

$$\varkappa_1(a_+ - \theta) = K_+(1 - a_+). \tag{18}$$

In the stationary case $j_2 = j_1$; $\varkappa_1(a_+ - \theta) = \varkappa_2\theta$. Introducing the effective coefficient of mass transfer through a gas layer $\varkappa_0$, we can write the following relationship between $\varkappa_0$, $\varkappa_1$, and $\varkappa_2$:

$$\frac{1}{\varkappa_0} = \frac{1}{\varkappa_1} + \frac{1}{\varkappa_2}.$$

The quantity $\varkappa_0$ depends on the convection intensity, i.e., $\varkappa_0 = \varkappa_0(R)$. Hence, it is easy to obtain the relationship

$$a_+ - \theta = \frac{\varkappa_0}{\varkappa_1}a_+.$$

Using (18) we obtain $\varkappa_0(R)\,a_+ = K_+(1 - a_+)$, from which

$$a_+ = \frac{K_+}{K_+ + \varkappa_0(R)}.$$

On the other hand, the macroscopic rate of the heterogeneous reaction is expressed in the well-known form [1]

$$W = \frac{K_+\varkappa_0(R)}{K_+ + \varkappa_0(R)}. \tag{19}$$

The influence of convection will evidently be most substantial in the diffusion range.

Let us use the method elucidated in [6] to determine the form of the function $\varkappa_0(R)$. The quantity $(\nu D/g\alpha)^{1/3}$ can be considered as some characteristic dimension of the domain not enclosed by the convection, i.e., the quantity $(\nu D/g\alpha)^{1/3}$ is proportional to the magnitude of the diffusion boundary layer δ.

In other words,

$$h/\delta = CR^{1/3}.$$

The constant C is determined easily from the following considerations. For $R = R_*$, $h = \delta$, i.e., $C = R_*^{-1/3}$ and $\delta = h(R_*/R)^{1/3}$. On the other hand, the diffusion Nusselt number Nu is determined by the expression $Nu = \varkappa_0 h/D$ or $Nu = h/\delta$. It hence follows that

$$\varkappa_0 = \frac{D}{h}\left(\frac{R}{R_*}\right)^{1/3}.$$

If it is taken into account that the diffusion Nusselt number is one for a horizontal layer, we can write

$$\varkappa_0 = \varkappa_1\left(\frac{R}{R_*}\right)^{1/3}, \qquad (20)$$

where $\varkappa_1 = D/h$ is the coefficient of mass transfer for a diffusion transfer mechanism. Using (20) and introducing the dimensionless macroscopic reaction rate $J = W/\varkappa_1$, let us rewrite (19) as

$$J = \frac{\gamma R^{1/3}}{R_*^{1/3}\gamma + R^{1/3}} \quad (R > R_*), \qquad (21)$$

wherein R_* is defined by (16). For $R \to R_*$, $J \to \gamma/(\gamma + 1)$. In the case of a purely diffusion mass transfer mechanism, it is necessary that $\gamma \gg 1$ $(J \sim 1)$ in order that the whole process be limited by diffusion. For $\gamma \ll 1$, $J \to \gamma$. Ordinarily, the temperature needed to accomplish the appropriate mode of reaction progress is selected from these conditions. The inequality $\gamma \gg (R/R_*)^{1/3}$ must be satisfied to accomplish the diffusion mode in the presence of convection. If the quantity $\gamma \approx 10$ in the absence of convection can be considered sufficient for the progress of the reaction in the diffusion range, then in the presence of convection γ becomes equal to the quantity $(R/R_*)^{1/3}$ already for $R \approx 10^6$. Such values of the Rayleigh number can easily be realized in tests. Thus, for example, a layer of height ≈3 cm is adequate to reach the number $R \simeq 10^6$ for the heterogeneous catalytic reaction of dimerization of ethylene.

NOTATION

ρ, density; μ_1, μ_2, molecular weight of the initial substance and weight of the reaction product; a, product concentration; a_+, product concentration on the boundary; T, temperature; β, coefficient of volume expansion; $\vec{v}$, velocity vector; t, time; z, vertical coordinate; ξ, dimensionless vertical coordinate; h, layer height; $\vec{g}$, gravitational acceleration vector; ν, coefficient of kinematic viscosity; p, pressure; D, coefficient of diffusion; Sc, Schmidt number; $R = (g\alpha/\nu D)h^3$, diffusion Rayleigh number; k_1, k_2, wave numbers along the horizontal axes; $\varkappa_1$, $\varkappa_2$, coefficients of mass transfer from the boundary to the volume and from the volume to the surrounding medium.

LITERATURE CITED

1. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics [in Russian], Nauka, Moscow (1967).
2. I. M. Mihaljan, Astrophys. J., 136, No. 2 (1962).
3. A. Pellew and R. V. Southwell, Proc. Roy. Soc., A176, 966 (1940).
4. G. Z. Gershuni and E. M. Zhukovitskii, Convective Stability of an Incompressible Fluid [in Russian], Nauka, Moscow (1972).
5. L. V. Kantorovich and V. I. Krylov, Approximate Methods of Higher Analysis [in Russian], Fizmatgiz, Moscow (1962).
6. V. V. Barelko and É. A. Shtessel', Inzh.-Fiz. Zh., 24, No. 1 (1973).